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(54) THERMOPLASTIC BLEND

(71) We, BORG-WARNER CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America of 200 South Michigan Avenue, Chicago, Illinois, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a thermoplastic blend of polymers. More particularly, this invention relates to a thermoplastic blend of polycarbonate, ABS graft polymer, and copolymer, which blend is suitable for use in place of metal components, such as those used in car bodies.

There are a great variety of ABS graft polymers prepared, such as those set forth in United States Patent 3,238,275. There are also graft polymer blends such as the blends of ABS graft polymers with alpha-methylstyrene-acrylonitrile copolymers of United States Patent 3,010,936. These compositions have been found useful for a variety of different end uses; however these compositions are considered somewhat flexible and not sufficiently impact resistant to be used in place of metallic elements, for example in car parts. It was decided to blend graft polymers, such as the ABS graft polymer mentioned above, with polycarbonate compositions in order to provide a thermoplastic blend having improved chemical and physical properties. Such a blend is set forth in United States Patent 3,130,177. In this patent the composition is that of polycarbonate with an ABS graft polymer. The ABS is essentially a graft polymer prepared by polymerizing acrylonitrile and styrene in the presence of a prepolymerized polybutadiene latex. The physical properties of this blend of ABS with polycarbonate are highly desirable for a variety of applications; however, the composition has the following drawbacks, namely that its heat distortion temperature, impact resistance and hardness are not sufficiently high to make it suitable in many applications in place of metal.

According to the present invention, there is provided a thermoplastic blend of polymers which comprises:

(A) from 10% to 50% by weight of the blend of a graft polymer prepared by polymerizing from 40 to 90% by weight of the graft polymer of a mixture composed of (1) at least one monovinyl aromatic hydrocarbon monomer which is styrene, alpha-methylstyrene, a vinyltoluene or an alpha-methylvinyltoluene and (2) at least one monomer which is a substituted or unsubstituted acrylonitrile, or a substituted or unsubstituted acrylic acid ester, in the presence of from 60% by weight to 10% by weight of the graft polymer of a prepolymerized polymeric conjugated diene homopolymer or a conjugated diene copolymer prepared from conjugated dienes copolymerized with at least one monomer which is a monovinyl aromatic hydrocarbon, a substituted or unsubstituted acrylonitrile, or a substituted or unsubstituted acrylic acid ester;

(B) from 80% by weight to 10% by weight of the blend of a copolymer prepared by copolymerizing (1) 10 to 40% by weight of the copolymer of at least one monomer which is a substituted or unsubstituted acrylonitrile or a substituted or unsubstituted acrylic acid ester with (2) from 90% by weight to 60% by weight of the copolymer of at least one monovinyl aromatic hydrocarbon which is styrene, alpha-methylstyrene, a vinyltoluene or an alpha-methylvinyltoluene, at least 50% by weight of which monovinyl aromatic hydrocarbon is α-methylstyrene; and

(C) from 10% by weight to 80% by weight of the blend of a polycarbonate.

The term "graft copolymer" is employed herein to designate the product formed by reacting a polymerizable monomer (or mixture of polymerizable monomers), under poly-

merizing conditions, in the presence of a previously formed polymer or copolymer.

Graft polymers suitable for use as component (A) of the blends of this invention may be prepared by the interaction, under polymerization conditions, of one or more components (A) (1), such as styrene, and one or more components (A) (2), such as acrylonitrile or methyl methacrylate with a latex of polybutadiene; or poly(butadiene-styrene), or poly(butadiene-acrylonitrile) copolymer.

Component (A) (2) preferably comprises from 5% to 30% by weight of the total (A) components (for example, acrylonitrile, styrene and polybutadiene), component (A) (1) preferably comprises from 25% to 85% by weight thereof.

The following is a description of the preparation of two representative graft polymers suitable for use in forming blends of this invention. "Parts" are parts by weight.

	X (parts)	Y (parts)
	(parts)	(parts)
Polybutadiene latex, polybutadiene equivalent	30.0	50.0
Acrylonitrile	25.0	15.0
Styrene	45.0	35.0
Cumene hydroperoxide	0.75	0.75
Sodium salt of hydrogenated disproportionated rosin	2.0	1.85
Sodium pyrophosphate	0.5	0.5
Sodium hydroxide	0.15	0.105
Sodium salt of condensed alkyl naphthalene sulfonic acid	0.15	
Dextrose	1.0	1.0
Ferrous sulfate	0.01	0.01
Water, including water present in the polybutadiene latex	160.0	182.0

Recipe X was introduced into a glass reactor which was sealed and tumbled for six hours in a water bath heated to 65° to 85°C. At the end of this time, reaction was essentially complete. The copolymer formed was recovered as follows: the final reaction mixture was coagulated with dilute brine and sulfuric acid, heated to 95°C. to produce partial granulation of the coagulated product to facilitate subsequent filtration and washing operations, filtered, washed and finally dried to constant weight at 110°C.

Recipe Y was charged into a pressure tight reactor. The reactor was placed in a water bath and heated to a temperature of 60°C. and maintained at this temperature under autogeneous pressure for a period of 85 minutes. At the end of this time, the reaction was essentially complete.

Certain physical properties of the graft copolymers prepared as above described are tabulated below:

Graft copolymer	X	Y
Tensile Strength, p.si.. 73°F	4,600	2,900
Tensile — Elongation, per cent	70	50
Deflection Temperature, °F, $\frac{1}{2}'' \times \frac{1}{2}'' \times 5$ bar, 66 p.s.i.	212	183
Deflection Temperature, °F, $\frac{1}{2}'' \times \frac{1}{2}'' \times 5''$ bar, 264 p.s.i.	192	160
Hardness Rockwell R	87	
Hardness — Shore D		64

Copolymers suitable for use as component (B) of the blends of this invention are prepared by the copolymerization of one or more of components (B) (1) with one or more of components (B) (2). The preferred components are acrylonitrile and alpha-methylstyrene.

Component (B) (1) preferably comprises from 20% to 30% by weight of the total (B) components. Component (B) (2) preferably comprises from 80% to 70% by weight of the total (B) components. Particularly suitable copolymeric blending components of this invention are obtained by using alpha-methylstyrene containing styrene, for example a copolymer (B) obtained from a mixture containing not less than 40% by weight of alpha-methylstyrene and up to 40% by weight styrene, especially from 80% to 60% of alpha-methylstyrene and from 5% to 15% by weight of styrene.

The following is a description of the preparation of a copolymer suitable for use in forming the blends of this invention.

Copolymers of alpha-methylstyrene and acrylonitrile and terpolymers of alpha-methylstyrene, styrene and acrylonitrile, may be prepared in accordance with the following recipes (set forth in parts by weight) and operating procedures.

While the ratios of alpha-methylstyrene, styrene, and acrylonitrile differ in the various recipes, the remaining components thereof are the same in all recipes both with respect to identity and amount. Also, the table provides the heat distortion point of various polymers formed.

Polymer designation	A	B	C	D	E	F
Alpha-methylstyrene	70	60	60	50	50	40
Styrene	0	7	10	20	30	40
Acrylonitirle	30	33	30	30	20	20
Heat distortion point, °C (Note A)	109	—	118.5	100	97.5	92.5
Potassium per sulfate	0.25					
Sodium hydroxide	0.1					
Dresinate 731 (Note B)	2.0					
Water	100.0					

NOTE A — A compression molded bar one inch wide, four inches long and 0.041 to 0.045 inch thick is employed as a test specimen in determination of heat distortion point. The test bar is carefully centered upon and forms a bridge between two supports, the knife edges of these supports being separated by a distance of 0.125 inch. A 30 g. weight is placed on the exact center of the so supported test bar. The resulting assembly is located in an air oven and heat (electrically generated) is applied at the rate necessary to secure a temperature rise of the air of 1°C. per minute. The temperature at which the bar falls from the supports is the heat distortion point of the polymer blend.

NOTE B — Dresinate 731 is the sodium salt of hydrogenated, disproportionated rosin.

The preparative procedure followed in the production of copolymer B (a terpolymer) will be described as exemplifying the procedure followed in the preparation of all copolymer and terpolymer blending components used in this invention.

The monomer reactants (alpha-methylstyrene, styrene and acrylonitrile) were emulsified in water which contained a small amount of sodium hydroxide and Dresinate 731. Potassium persulfate catalyst was then added, and the reaction vessel was sealed and placed in a water bath heated to 80° to 85°C. The reaction vessel was tumbled in the water bath at the temperature given until reaction was about 90% complete at which time the vessel was removed from the water bath, opened, and an additional 0.125 parts by weight potassium persulfate catalyst was added. The reaction vessel was resealed and again placed in the water bath (heated to the temperature previously given) and tumbling of the reactor therein was continued until the polymerization reaction was essentially complete. In the preparation of the terpolymers of this example, the total reaction time was five hours. In the preparation of resin B, the yield of terpolymer was 98.0% of theory.

In many instances the polymer latex formed as the result of these operations may be employed in the subsequent blending step. However, if it is desired to recover the polymer formed, the polymer latex produced is coagulated by treatment with a solution of an electrolyte such as dilute brine or dilute sulfuric acid. The resulting coagulated mixture is preferably heated to about 95°C. to bring about partial granulation of the coagulum, thus facilitating subsequent filtering and washing operations. The coagulum is separated by filtration, is washed with water and then dried to constant weight at 110°C.

It will be noted that with a single exception (polymer A) all of the above recipes include styrene in addition to alpha-methylstyrene. In contrast to alpha-methylstyrene, the emulsion polymerization of styrene proceeds at a rapid rate. In addition, the presence of a small amount of styrene greatly accelerates the rate of emulsion polymerization of alpha-methylstyrene. Accordingly, it is advantageous to employ a styrene and alpha-methylstyrene mixture in order to accelerate the emulsion polymerization reaction. However, and confining attention to the binary styrene alpha-methylstyrene mixture, preferably this contains about 5 to 15% styrene, based on the weight of the copolymer.

The preferred polycarbonates suitable for use as component (C) of the present invention are made by converting di-(mono-hydroxyphenyl)-substituted aliphatic hydrocarbons with phosgene in a manner well known in the art. For example, British Patent 772,627 discloses suitable examples of the di-(monohydroxyphenyl)-substituted aliphatic hydrocarbons and the methods of converting these materials to polycarbonates. A typical polycarbonate for utilization in the present invention is the polycarbonate of 2,2-bis-(4-hydroxyphenyl)-propane, which polycarbonate has the following properties:

Izod impact strength, ft.lb./inch notch 1/8″ bar	14.8
Tensile strength, p.s.i., 73°F.	8,800
Tensile elongation, percent	60
Hardness, Rockwell	125
Melt index, 410°F.[1]	.3Al
Deflection temperature, °F., 1/2″×1/2″×5″ bar, 66 p.s.i.	291
Deflection temperature, °F., 1/2″×1/2″×5″ bar, 264 p.s.i.	273

[1]Modification of the procedure set forth in A.S.T.M. Method D—1238—52T. This procedure was originally developed for determining the melt index of polyethylene. In this method, the weight in grams of polyethylene that is discharged during a period of three minutes through a standard orifice positioned below a reservoir of the polymer that is at a standard temperature and under a standard pressure is determined. This determination is proportioned to give the grams of polymer discharged during ten minutes which figure is, by definition, the melt index of polyethylene.

Since the thermoplasticity of the blends with which this invention is concerned is not even of the same order of magnitude as that of polyethylene, a considerably modification of the standard conditions and dimensions set forth in A.S.T.M. Method D—1238 had to be made in order to make this general method applicable to the blends with which this invention is concerned. These modifications involved changes in the size of the orifice, the pressure applied to the plastic in the reservoir and the reservoir temperature.

As used herein, melt indexes express the weight in grams of polymer blend discharged in one minute through an orifice 0.125 inch

in diameter and 0.315 inch long from a reservoir 0.373 inch in diameter containing polymer maintained at a temperature of 410°F. and under a pressure produced by a 5664 g. load. Thus, a melt index of .3A1 means that .3 g. of polymer were discharged through the orifice in one minute under the conditions named. Similarly, a melt index of .1A3 means that .1 g of polymer was dicharged through the orifice in three minutes under the named conditions.

Other suitable polycarbonates may be prepared from the following diphenols: bis - (4-hydroxyphenyl) - methane; 3,3 - bis - (4-hydroxyphenyl) - cyclohexane; 2,2 - bis - (4-hydroxyphenyl) - butane; 2,2 - bis - (4-hydroxyphenyl) - pentane; 2,2 - bis - (4-hydroxyphenyl) - hexane; 2,2 - bis - (4-hydroxyphenyl) - heptane, 2,2 - bis - (2,6-dichloro - 4 - hydroxyphenyl) - propane; 2,2-bis - (2,6 - dibromo - 4 - hydroxyphenyl)-propane. The graft polymer composition designated Y above was blended with the copolymer designated B and a polycarbonate sold under the tradename LEXAN by the General Electric Company. The LEXAN polycarbonate is a polycarbonate of 2,2 - bis-(4 - hydroxyphenyl) - propane prepared by reacting bisphenol A with phosgene.

The following Examples illustrate blends of the invention. Parts are by weight.

Example	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Copolymer B	80	70	60	50	40	30	20	10	70	60	50	40	30	20
Graft Copolymer Y	10	10	10	10	10	10	10	10	20	20	20	20	20	20
Polycarbonate LEXAN*	10	20	30	40	50	60	70	80	10	20	30	40	50	60
Ethylene oxide-polypropylene glycol (lubricant)	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5
Tensile Strength (ultimate) ASTM D338—61T	8850	9200	8900	8900	8700	8400	8400	9600	7650	7900	7900	7650	7650	7500
Elongation (%)	25	30	104	80	130	126	80	170	30	25	20	20	20	55
Tensile Modulus ($\times 10^5$)	4.4	4.2	4.3	3.8	3.9	3.4	3.6	3.3	3.9	4.0	3.8	3.5	3.4	3.3
Notched Izod Impact (IM) D-256-56 Method C	.7	1.7	4.0	8.3	10.5	12.6	15.8	16.4	1.8	5.5	7.4	8.9	9.0	11.8
Melt Index @ 450°F	.7	.7	.8	.8	.7	.7	.8	.9	.5	.5	.6	.6	.8	.8
Hardness R Scale	117	118	116	118	118	118	119	118	114	114	115	115	115	114
L Scale	96	96	95	96	96	95	97	95	98	88	88	88	88	87
HDP Ann. ** @ 16 psi	248	253	259	265	270	271	279	275	250	249	251	255	264	264
HDP Unan. @ 264 psi	223	228	230	227	237	237	246	250	224	219	224	222	226	230
HDP Ann. ** @ 264 psi	241	243	247	248	244	252	264	268	235	241	241	239	243	252

* TM of 2,2-bis-(4-hydroxyphenyl)-propane polycarbonate sold by General Electric Company.
** Annealing was accomplished by placing the sample in an air circulating oven under given load at its yield point temperature

Example	15	16	17	18	20	20	21	22	23	24	25	26	27
Copolymer B	10	60	50	40	30	20	10	50	40	30	20	10	40
Graft Copolymer Y	20	30	30	30	30	30	30	40	40	40	40	40	50
Polycarbonate LEXAN*	70	10	20	30	40	50	60	10	20	30	40	50	10
Ethylene oxide-polypropylene glycol (lubricant)	.5	.5	.6	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5
Tensile Strength (ultimate) ASTM D638—61T	7300	6900	6750	6900	6750	6500	7100	6500	6400	6200	6000	5700	5800
Elongation (%)	45	35	20	40	100	105	130	50	15	10	20	20	100
Tensile Modulus ($\times 10^5$)	3.2	3.5	3.3	3.2	3.1	2.9	2.9	3.2	3.2	2.9	2.7	2.6	2.9
Notched Izod Impact (IM) D—256—56 Method C	10.8	5.5	5.7	10.0	10.8	11.0	13.1	8.0	8.0	7.6	9.5	9.2	7.3
Melt Index @ 450°F	.9	$.4A_1$	$.4A_1$	$.5A_1$	$.5A_1$	$.6A_1$	$.6A_1$	$.9A_3$	$.9A_3$	$1.2A_3$	$1.1A_3$	$.4A_1$	$.3A_3$
Hardness R Scale	112	108	108	108	109	109	111	103	102	103	103	102	97
L Scale	84						79						
HDP Ann **@ 16 psi	268	241	246	249	253	264	264	246	245	249	250	255	242
HDP Unan. @ 264 psi	230	215	211	215	221	226	230	215	212	218	208	205	212
HDP Ann .**@ 264 psi	255	233	232	237	244	234	246	231	231	233	230	230	224

*TMof 2,2-bis-(4-hydroxyphenyl)-propane polycarbonate sold by General Electric Company.
**Annealing was accomplished by placing the sample in an air circulating oven under given load at its yield point temperature.

The polybutadiene latex utilized in component (A) of the blends of this invention may be replaced in part or entirely by other conjugated diolefine polymer latices. In the preparation of such latices, the butadiene may be replaced in part or entirely by such conjugated diolefines as isoprene, pentadiene-1,3; methyl 1,3-pentadienes; dimethyl butadiene-1,3; the 1,3 and 2,4-hexadienes including mixtures of one or more conjugated diolefines including butadiene. As indicated previously, the backbone substrate of the graft copolymer may be a copolymer wherein the aforementioned conjugated dienes are copolymerized with a monovinyl aromatic hydrocarbon such as styrene, alpha-methylstyrene, vinyltoluene, alpha-methylvinyltoluenes; or nitriles or esters of acrylic acid or substituted acrylic acid; or mixtures thereof.

The graft polymer and copolymer both utilize monovinyl aromatic hydrocarbons, with styrene and α-methyl styrene being prepared. Other monomers that may be used in place of acrylonitrile include methacrylonitrile and ethacrylonitrile, and acrylic acid esters such as methylmethacrylate and ethylacrylate.

The general field of utility of the resin blends in this invention is as components that require high impact resistance and high heat distortion temperatures and the compositions find their greatest usefulness in the fabrication of shaped articles that are subjected to stress during assembly and which may subsequently be subjected to vibration, shock, impact loads and the like during use. The blends of this invention are also well adapted for the fabrication of calendered rigid sheets, moldings, pipes, pipe fittings, valves and valve parts. The unusually favorable properties of these blends permit them to be fabricated into articles that exhibit one or more directional transitions in their design. The rigid articles that may be made from these blends may be tapped, drilled, threaded, etc. The excellent chemical resistance of these blends and their resistance to deterioration also makes it possible to utilize the blends for the fabrication of plastic conduit and pipe for transporting corrosive fluid at elevated pressures and temperatures.

WHAT WE CLAIM IS:—

1. A thermoplastic blend of polymers which comprises:

(A) from 10% to 50% by weight of the blend of a graft polymer prepared by polymerizing from 40 to 90% by weight of the graft polymer of a mixture composed of (1) at least one monovinyl aromatic hydrocarbon monomer which is styrene, alpha-methylstyrene, a vinyltoluene or an alpha-methylvinyltoluene and (2) at least one monomer which is a substituted or unsubstituted acrylonitrile, or a substituted or unsubstituted acrylic acid ester, in the presence of from 60% by weight to 10% by weight of the graft polymer of a prepolymerized polymeric conjugated diene homopolymer or a conjugated diene copolymer prepared from conjugated dienes copolymerized with at least one monomer which is a monovinyl aromatic hydrocarbon, a substituted or unsubstituted acrylonitrile, or a substituted or unsubstituted acrylic acid ester;

(B) from 80% by weight to 10% by weight of the blend of a copolymer prepared by copolymerizing (1) 10 to 40% by weight of the copolymer of at least one monomer which is a substituted or unsubstituted acrylonitrile or a substituted or unsubstituted acrylic acid ester with (2) from 90% by weight to 60% by weight of the copolymer of at least one monovinyl aromatic hydrocarbon which is styrene, alpha-methylstyrene, a vinyltoluene or an alpha-methylvinyl toluene, at least 50% by weight of which monovinyl aromatic hydrocarbon is α-methylstyrene; and

(C) from 10% by weight to 80% by weight of the blend of a polycarbonate.

2. A blend according to claim 1 wherein component (A) (1) comprises from 25 to 85% by weight of the total graft polymer composition and component (A) (2) comprises from 5% to 30% of the total graft polymer composition.

3. A blend according to claim 1 or 2, wherein the copolymer comprises from 20 to 30% by weight acrylonitrile, 80 to 60% by weight alpha-methylstyrene and 5 to 15% by weight styrene.

4. A blend according to claim 1 or 2, wherein the copolymer comprises from 20 to 30% by weight acrylonitrile and from 80 to 70% by weight alpha-methylstyrene.

5. A blend according to any of the preceding claims, wherein the graft polymer contains a polybutadiene substrate.

6. A blend according to any of claims 1 to 4, wherein the graft polymer contains a poly-(butadiene-styrene) substrate.

7. A blend according to any of claims 1, 2, 4 and 5, wherein the graft polymer is prepared by polymerizing styrene and acrylonitrile in the presence of polybutadiene and the copolymer is prepared by copolymerizing acrylonitrile with alpha-methyl styrene.

8. A blend according to claim 1, wherein the graft copolymer is prepared by polymerizing from 25% by weight to 85% by weight styrene and 5 to 30% by weight acrylonitrile in the presence of from 10 to 60% by weight polybutadiene and wherein the copolymer is prepared by copolymerizing 20 to 30% by weight acrylonitrile with 80% by weight to 60% by weight alpha-methylstyrene and 5 to 15% by weight styrene.

9. A blend according to any of the preceding claims, wherein the polycarbonate is prepared by reacting 2,2-bis-(4-hydroxyphenyl)-propane with phosgene.

10. A blend according to any of claims 1 to 8, wherein the polycarbonate is prepared

by reacting bis - (4 - hydroxyphenyl) methane, or 2,2 - bis - (2,6 - dibromo - 4 - hydroxyphenyl) - propane with phosgene.

11. A thermoplastic blend according to claim 1 substantially as hereinbefore described.

12. A process for the preparation of a thermoplastic blend as defined in claim 1 substantially as hereinbefore described.

13. A thermoplastic blend obtained by a process according to claim 12.

14. Shaped articles obtained from a thermoplastic blend according to any one of claims 1 to 11 or 13.

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